RELATION BETWEEN FUEL PROPERTIES AND CHEMICAL COMPOSITION. II. CHEMICAL CHARACTERIZATION OF U.S. NAVY SHALE-II FUELS

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As domestic and imported petroleum supplies dwindle and petroleum increases dramatically in cost, it is imperative for the Navy to consider future liquid fuel options. The Navy has two thrusts in transportation fuels: (a) explore the relaxation of fuel specifications and (b) examine alternate sources of fuels. This paper deals with one of the alternate sources, shale oil.

The bulk of the Navy's vehicles utilize middle distillate fuels; a kerosene type jet fuel, JP-5, for aircraft and diesel fuel marine (DFM) for ships and boats. Reasonable yields of these fuels can be obtained from shale oil. Further, shale crude oil has a good hydrogen content which allows upgrading to finished fuel with modest additions of expensive hydrogen. Thus the interest in Navy fuels from shale oil.

The Navy has completed two crude production/refining exercises with shale. The first of these, a 10,000 barrel operation (Shale-I), is described in two reports (1,2). The second, a 73,000 barrel operation (Shale-II), was completed in 1979 at the Toledo refinery of Sohio (3). This paper describes the chemical characterization of the JP-5 and DFM from the Shale-II project.

EXPERIMENTAL

Samples - One gallon samples of the various refinery streams were obtained from Sohio throughout the approximately one month of production. Periodic samples of finished JP-5 and DFM were also obtained during the acid treatment process which was completed subsequent to the hydrocracking and fractionation steps. Drum samples of the finished homogeneous JP-5 and DFM products were also examined.

Total Nitrogen - The fuel samples were pyrolyzed/combusted at 1000°C in a flow of argon/oxygen and the chemiluminescence for the reaction of NO with ozone measured (4). Types of specific nitrogen compounds found will be discussed in another paper of this symposium.

GC Analyses - The *n*-alkanes in the fuel samples were determined with a 100 meter OV-101 wall coated glass capillary column. The inlet split ratio was 50:1, the column oven was temperature programmed from 80 to 240°C, and the inlet temperature was 310°C.

LC Separation - Preparative scale liquid chromatography was performed with Waters PrepPak radially compressed silica columns. Fuel charges of 6 to 10 ml were carried through the column with *n*-pentane at a flow of 200 ml/minute. Refractive index, 254 nm ultraviolet, and 313 nm ultraviolet detectors monitored the LC effluent and keyed the collection of fractions.

Mass Spectrometry - Electron impact mass spectrometry was done at NRL on the effluent from a 6 ft. OV-101 packed GC column programmed from 70 to 210°C. Field ionization mass spectrometry (FIMS) was performed by SRI International on contract to NRL. In this latter analysis, the fuel sample was frozen on a solids inlet probe prior to insertion into the mass spectrometer. The spectra accumulated for each mass during a temperature program were normally totaled for data presentation (5). Molecules boiling below 140°C are lost or depleted with this technique but such compounds comprise a very small fraction of JP-5 or DFM. Since the ionization efficiency for hydrocarbon classes is currently under study, the FIMS data is utilized primarily in a qualitative sense.

NMR Examination - Fuel samples and fractions were analyzed by proton and ^{13}C NMR at the Naval Biosciences Laboratory. The spectra were taken on a Varian FT-80A. Chromium acetonyl acetonate was added as a relaxation reagent.

RESULTS

Nitrogen Content - The bulk of the shale oil nitrogen was removed in the hydrocracking step. All four products from fractionation of the hydrocrackate--naphta, jet, diesel and heavy oil--contained substantial amounts of nitrogen, however. The data in Table I indicate that the lighter products had less total nitrogen.

All products increased in nitrogen content as the refining run progressed. For instance, the 25 day hydrocrackate contained 2 1/2 times the nitrogen found in the 12 day product. The jet and diesel fractions almost doubled in nitrogen over the same time span. The hydrocracking catalyst lost activity throughout the run.

The nitrogen content of the JP-5 and DFM fractions, the products important to the Navy, was too high to afford satisfactory stability. Extensive acid treatment with sulfuric acid reduced the nitrogen content in the finished fuels, however, to one ppm(w/v) for the JP-5 and 18 ppm (w/v) for DFM.

n-Alkane Content - Shale fuels exhibit higher freeze and pour points than similar fuels made from most petroleum crudes. This is related to the symmetrical n-alkane molecules which are major components of shale derived fuels (6). The content of these molecules in the Shale-II middle distillate fuels is listed in Table II. The relationship between freezing point and composition will be considered in another paper of this symposium.

FIMS Fingerprint - Field ionization mass spectrometry of a mixture affords a spectrum of the molecular ions since fragmentation is minimal. Thus a distribution of molecular sizes and hydrocarbon classes can be obtained from a single analysis. This is illustrated in Figures 1 and 2 which compare the FIMS fingerprints for JP-5 from Shale-I and Shale-II refining. Distinct differences can be noted. The preponderance of alkanes (C_nH_{2n+2}) is highlighted in Shale-I fuel which was produced by cracking the shale crude by delayed coking. Shale-II, a hydrocracking process, produced a product much lower in alkanes. Analysis for total n-alkane content agrees with this finding, 37% in Shale-I JP-5 (6) and 22% for Shale-II. Other significant differences between the two jet fuels can be noted in the much higher peaks for substituted benzenes (C_nH_{2n-6}) and tetralins (C_nH_{2n-8}) in the Shale-II product.

Other differences can be noted in the FIMS data assembled in Table III. For instance, Shale-II also has higher peak sums for monocyclic alkanes (C_nH_{2n}) and dicyclic alkanes (C_nH_{2n-2}) than Shale-I (coking). Data for a third JP-5 sample, a ten gallon quantity produced by fractionation of Paraho shale crude followed by 1200 psi catalytic hydrogenation of the jet fuel cut (7), is also shown in Table III. Again this fuel has a distinctly different FIMS fingerprint in response to the refining process used.

Preparative Scale LC - Separation of JP-5 and DFM on the Waters radially compressed silica column gave many fractions. This is illustrated in Figure 3 for six ml of DFM. Fraction one, beginning at 3.2 min, is the saturate fraction which was detected with a refractive index detector. Fraction 2, indicated by slight absorption on the 254 nm uv detector, corresponds to the olefin fraction. The subsequent fractions, as indicated by the strong absorption on one or both of the uv detectors, are comprised of aromatic fractions. It is noteworthy that fractions 7,8 and 9 exhibit significant absorption at 254 nm but none at 313 nm. The JP-5 sample gave only five fractions in the same type of analysis.

Evaporation of the n-pentane solvent gave an estimate of the amount of the various fractions. The percentages normalized to total 100% are listed in Table IV. Recoveries of input sample amounted to 96 and 93% for the DFM and JP-5, respectively. The losses were due to evaporation of volatile components during the removal of the solvent. As expected, fractions 1 and 3 comprised the bulk of the fuel samples, 88.5% of the DFM and 95.3% of the JP-5.

Mass Spectrometry of LC Fractions - The fractions from the preparative scale LC were subjected to GC/MS analysis with electron impact ionization. The total fractions were also analyzed by field ionization mass spectrometry with a direct insertion probe. The FIMS m/e plot for DFM fraction five is depicted in Figure 4. The two major hydrocarbon series observed in this fraction are C_nH_{2n-12} and C_nH_{2n-14}, naphthalene and acenaphthenes. Trace amounts of the C_nH_{2n-10} and C_nH_{2n-8} series also appear in Figure 4.

A summary of the hydrocarbon series in the nine DFM and five JP-5 LC fractions are listed in Table V. The data are qualitative in nature and based on both MS techniques, EI and FI. The trends with fraction number are as expected, hydrocarbons with less hydrogen appear in the later fractions. Further, the trend in aromatic ring size was 1 ring (fraction 3), 2 rings (fraction 4), and 3 rings (fractions 5-9). The JP-5 has very little three ring material but the DFM exhibits evidence for considerable amounts of acenaphthenes, fluorenes, and phenanthrenes/anthracenes.

The LC separation did not give sharp separation by ring size, however. For instance, tetralins appeared in fractions 3-5 and naphthalens occurred in fractions 4-7. Larger molecules in a particular series eluted in later fractions.

Significant amounts of partially or fully saturated ring compounds were found in the jet and diesel products. Mono- and dicyclic alkanes were a major portion of the saturate fraction and a fair amount of tricyclic alkanes were also found. Tetralins/indanes were also found in abundance. Some partially hydrogenated tricyclic aromatics -- C_nH_{2n-10} (tetrahydroacenapthene, hexahydrofluorene, and octahydrophenanthrene) -- were also observed. The presence of these types of compounds is evidence of the high pressure hydrocracking step in the refining process.

NMR analyses - Fraction 3 from the LC separation was subjected to proton nmr examination. The information from this examination was treated by the method of Clutter and co-workers (8) to describe the average molecule. The calculated parameters are summarized in Table VI. The values obtained are consistent with the other information in this paper and in the description of the Shale-I JP-5 reported in an earlier article (6).

CONCLUSIONS

The information presented in this paper shows that shale oil has an excellent potential as a source for high quality middle distillate fuels. The composition of such fuels may vary widely, however, depending on the overall refining process. Much work is needed to explore other refining options and to examine the effect of refining on finished fuel composition and properties.

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TABLE I. Shale-II Refining Nitrogen Content*

	Product				
Days of Operation	Hydro-crackate	Naphtha	Jet Pre-Acid	DFM Pre-Acid	Fractionation Residue
12	1400	---	1700	2500	1940
18	2000	---	2300	2900	2700
21	3000	640	2500	4000	----
25	3800	---	2900	4700	----

* - PPM (wt/vol).
Crude shale oil contained 2.1% nitrogen

TABLE II. n-Alkanes in Shale-II Fuels

n-Alkane	Weight Percent JP-5	Weight Percent DFM
C_8	---	0.06
C_9	0.14	0.13
C_{10}	4.20	0.46
C_{11}	7.23	0.93
C_{12}	6.08	1.40
C_{13}	3.30	2.22
C_{14}	0.93	2.39
C_{15}	0.28	2.61
C_{16}	0.06	2.19
C_{17}	0.01	2.11
C_{18}	---	1.40
C_{19}	---	0.65
C_{20}	---	0.04
Total	22.23	16.59

TABLE III. Hydrocarbon Classes in JP-5 Samples by FIMS*

Hydrocarbon Series	Shale-I (Coking)	Shale-II (Hydrocracking)	Shale-I (Fractionation & Hydrogenation)
C_nH_{2n+2}	50.8	30.4	40.6
C_nH_{2n}	12.2	16.9	20.8
C_nH_{2n-2}	4.1	7.1	11.2
C_nH_{2n-4}	1.9	0.8	3.2
C_nH_{2n-6}	16.6	19.6	14.4
C_nH_{2n-8}	12.2	23.8	7.3
C_nH_{2n-10}	1.7	1.0	2.2

* Ion intensities (total = 100)

TABLE IV. Yields From LC Separation

	Percent Yield	
FRACTION	DFM	JP-5
1	68.9	73.6
2	0.8	2.9
3	19.6	21.7
4	7.1	1.6
5	1.2	0.3
6	0.6	---
7	0.7	---
8	0.5	---
9	0.7	---
% recovered	96	93

TABLE V. Hydrocarbon Series in Shale-II Fuels

MASS Series	LC Fraction* 1	2	3	4	5	6	7	8	9
2n + 2	J(M),D(M)	J(t),D	---------	--------	--------	------	-------	-------	-------
2n	J(M),D(M)	J ,D(M)	---------	--------	--------	------	-------	-------	--------
2n - 2	J(M),D(M)	J(M),D(M)	---------	--------	--------	------	-------	-------	--------
2n - 4	J ,D	J(M),D(M)	---------	--------	--------	------	-------	-------	--------
2n - 6	J(t),D(t)	J ,D(M)	J(M),D(M)	J ,D(t)	J(t)	------	-------	-------	--------
2n - 8	---------	J(t),D	J(M),D(M)	J(M),D(M)	J(t),D(t)	------	-------	-------	--------
2n - 10	---------	---- D(t)	J(t),D	J ,D(M)	J ,D(t)	D(t)	D(t)	-----	-------
2n - 12	---------	---------	J(t),D(t)	J(M),D(M)	J(M),D(M)	D(M)	D(t)	D(t)	D(t)
2n - 14	---------	----------	---------	J(t),D	J(M),D(M)	D(M)	D(M)	D(M)	D(M)
2n - 16	---------	----------	---------	---------	---- D(t)	D(t)	D(M)	D(M)	D(M)
2n - 18	---------	----------	---------	---------	---------	D	D(M)	D(t)	----

* J - present in JP-5 D - present in DFM
J(M) - major series in JP-5 D(M) - major series in DFM
J(t) - trace amount in JP-5 D(t) - trace amount in DFM

TABLE VI. Average Molecule in Fraction Three

Parameter	JP-5	DFM
Aromaticity	0.49	0.39
Aromatic Rings/ Molecule	1.0	1.0
Average Mol. Wt.	164	206
Average Mol. Formula	$C_{12.2}H_{16.8}$	$C_{15.2}H_{23.3}$
Alkyl Substituents/ Molecule	3.2	3.1
Carbons/Alkyl Substituent	2.0	3.0
Naphthene Rings/ Molecule	0.5	0.7

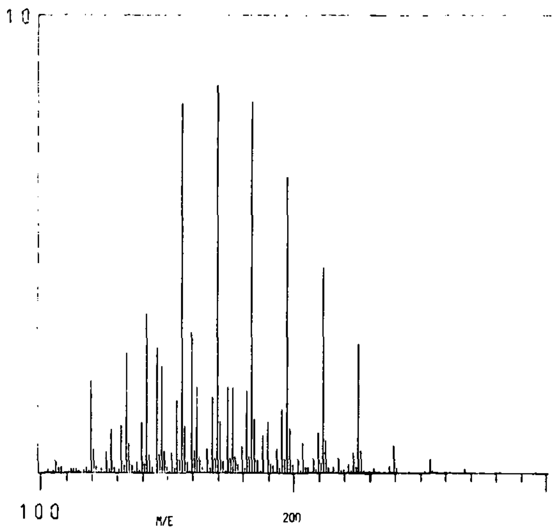

FIG. 1. FIELD IONIZATION MASS SPECTRUM OF SHALE-I JP-5.

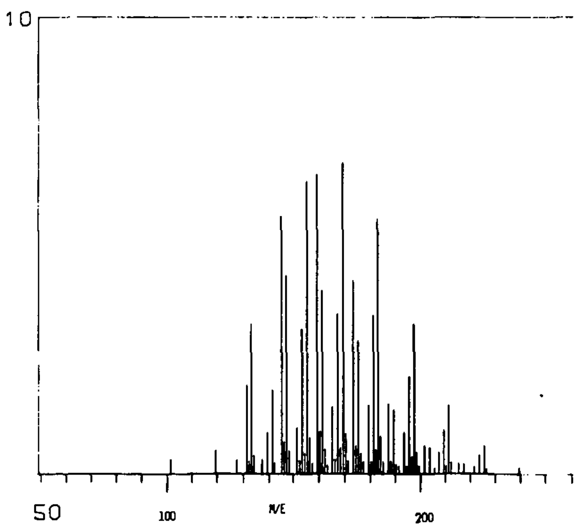

FIG. 2. FIELD IONIZATION MASS SPECTRUM OF SHALE-II JP-5.

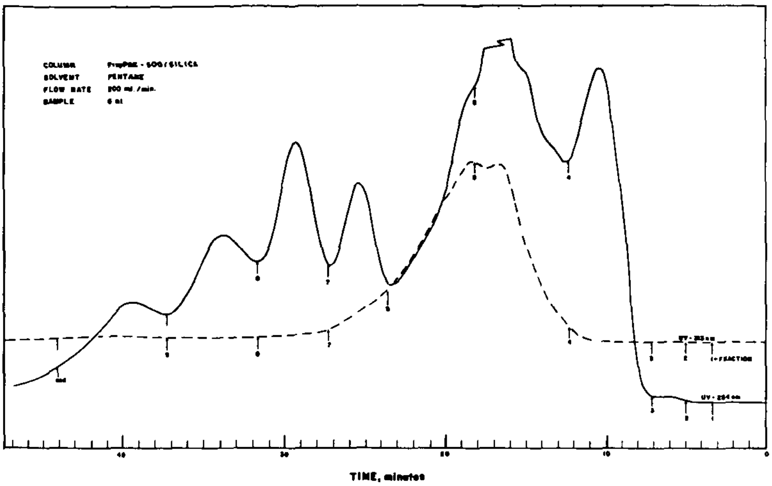

Fig. 3. Preparative scale LC separation of shale diesel fuel marine; solid line - 254 nm UV dectector, dotted line - 313 nm UV detector, RI detector trace not shown; small numbers indicate times when fraction collection was begun.

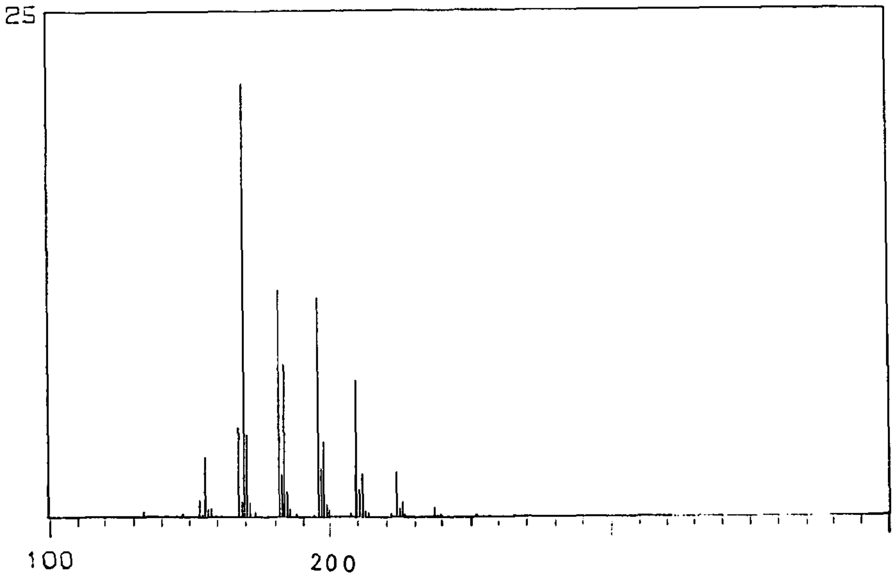

Fig. 4. Field ionization mass spectrum of diesel fuel marine, fraction 5. Major hydrocarbon series are C_NH_{2N-12} and C_NH_{2N-14}.